



ADMINISTRATIVE RECORD

SF FILE NUMBER

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planners
economists
scientists

1265412 - R8 SDMS

June 8, 1984

W68230.R4.41

California Analytical
Laboratories, Inc.
2544 Industrial Boulevard
West Sacramento, California 95691

Attention: Mr. Mark Masino

Gentlemen:

Subject: USEPA Contract Laboratory Request
ASARCO, Montana RI/FS

Attached is revision 2 for the ASARCO, Mt RI/FS soil/crop investigation (when will they ever stop?) I apologize again, however, if the laboratories would stop asking such good questions, I will stop revising the request. In all seriousness, I appreciate the laboratory questions as they have helped produce a testing program that is not only economical but also meeting the site investigation objectives.

Sincerely,

A handwritten signature in cursive script, appearing to read "Doug W. Lovell".

Douglas W. Lovell, P.E.
Site Project Manager

DEASARCO/sr065

cc: Keith Schwab/USEPA, Denver
Gene Taylor/USEPA, SMO, Helena
Bob Davis/CH2M HILL, Denver
Diane Shoup/CH2M HILL, Reston
Paula Ausserer/USEPA, CLP, SMO, Alexandria
Gaynor Dawson/Battelle, Richland
Doug Dollhopf/MSB, Bozeman



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0150646

June 8, 1984

W68230.R4.41

Chemtech Consulting Group, Ltd.
360 West 11th Street
New York, New York 10014

Attention: Mr. Alan Schoffman

Gentlemen:

Subject: USEPA Contract Laboratory Request
ASARCO, Montana RI/FS

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June 8, 1984

W68230.R4.41

Rocky Mountain Analytical Lab., Inc.
5530 Marshall Street
Arvada, Colorado 80002

Attention: Mr. Tony Maiorana

Gentlemen:

Subject: USEPA Contract Laboratory Request
ASARCO, Montana RI/FS

Attached is revision 2 for the ASARCO, Mt RI/FS soil/crop investigation (when will they ever stop?) I apologize again, however, if the laboratories would stop asking such good questions, I will stop revising the request. In all seriousness, I appreciate the laboratory questions as they have helped produce a testing program that is not only economical but also meeting the site investigation objectives.

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Douglas W. Lovell, P.E.
Site Project Manager

DEASARCO/sr065

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Gaynor Dawson/Battelle, Richland
Doug Dollhopf/MSB, Bozeman



0150648

June 8, 1984

W68230.R4.41

Versar, Inc.
6850 Versar Center
Springfield, Virginia 22151

Attention: Mr. Bill Nivens

Gentlemen:

Subject: USEPA Contract Laboratory Request
ASARCO, Montana RI/FS

Attached is revision 2 for the ASARCO, Mt RI/FS soil/crop investigation (when will they ever stop?) I apologize again, however, if the laboratories would stop asking such good questions, I will stop revising the request. In all seriousness, I appreciate the laboratory questions as they have helped produce a testing program that is not only economical but also meeting the site investigation objectives.

Sincerely,

A handwritten signature in cursive script, reading "Douglas W. Lovell", is positioned above the typed name.

Douglas W. Lovell, P.E.
Site Project Manager

DEASARCO/sr065

cc: Keith Schwab/USEPA, Denver
Gene Taylor/USEPA, 8MO, Helena
Bob Davis/CH2M HILL, Denver
Diane Shoup/CH2M HILL, Reston
Paula Ausserer/USEPA, CLP, SMO, Alexandria
Gaynor Dawson/Battelle, Richland
Doug Dollhopf/MSB, Bozeman

Revision 2; June 8, 1984

CASE ASSIGNMENT REQUEST

SOIL/CROP INVESTIGATION
PHASE 1 RI
ASARCO, MONTANA RI/FS
(EAST HELENA SMELTER)
71.8L30.0
EAST HELENA, MONTANA
EPA REGION VIII

SAS CONTROL NO: 1154H
CASE NO.: 2890

CH2M HILL
June 1, 1984
W68230.R4.41
Revision 1;
June 7, 1984

LIST OF QUESTIONS AND ANSWERS

11. Q: What is the crop holding time if samples are refrigerated/frozen upon laboratory receipt?
- A: 7 days
12. Q: What sample quantities will be sent to the laboratories for Method 14, Particle Size Analysis of Soils?
- A: Typically 2 - 16 oz. jars, the laboratory should analyze the total quantity received or the quantity called for in the ASTM specification, whichever is less.
13. Q: Method 11, Total Organic Matter in Soils calls for two determinations, are both necessary?
- A: Upon further examination of the Xeroxed method, a suitable and less expensive method is preferred, see the attached revised method.
14. Q: May a slurry pH determination be substituted for the saturated paste determination specified in Method 15, Soil pH?
- A: No
15. Q: Is a moisture content determination necessary for Method 9, Carbonate in Soils?
- A: Yes, the moisture content should be determined first, before the carbonate analysis.
16. Q: Can the laboratories be supplied with a complete copy of Method 16, X-Ray Diffraction of Soils?
- A: Yes, I have requested Battelle to send a copy to each lab, express mail today.
17. Q: Will RAS results have to be summarized on the specified (but as yet undisclosed) summary table?
- A: No, RAS results should be reported on standard CLP summary sheets.
18. Q: Is a standard kitchen blender a suitable substitute for the Wiley-type mill specified in Method 1, General Preparation for Crops?
- A: No, this may cause uneven breakdown and segregation of plant tissue besides not being made of stainless steel.

19. Q: May ICP be substituted for flame photometer?

A: Yes

DEASARCO/066

20. Q: How may the laboratory holding time for soils be extended beyond the one day specified?

A: Upon receipt by the laboratory, soils may be frozen at or below 2°C for a period of 21 days.

21. Q: Are you sure you need all sieves plus hydrometers on all soil samples as specified in Method A. Particle Size Analysis of soils

A: No, I'm not sure. Chances are we will not need all sieves and hydrometers on all soil samples. The necessary sieves have been respecified in the attached list of revisions. The need for hydrometer analysis will be made in the field. The laboratories, therefore need to submit



SUBJECT _____

BY _____ DATE _____

SHEET NO. _____ OF _____

PROJECT NO. _____

bids for (a) sieve and hydrometer, and (b) sieve only. For estimating purposes, $\frac{2}{3}$ of the samples may be assumed to be category (a) and the remaining category (b).

22. Q: The detection limits specified in Revision 1 for Method 2, Total Metals in Crops; Method 6, DTPA Extractable Metals in Soils; and Method 7, HCl Extractable Arsenic in Soils are unobtainable for some of the elements specified. What are we to do?

A: See the list of revisions in this request.

LIST OF REVISIONS*in Soils*

12. Method 11, Total Organic Matter has been replaced with the attached.
13. The SAS Control No. given previously was incorrect, the correct No. is 1154H.

DEASARCO/067



SUBJECT _____

BY _____ DATE _____

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14. The required sieve sizes for Method 14, Particulate Size Analysis of Soils are:

3-in

1-in

3/8-in

No. 4

No. 8 or No. 10

No. 20 or No. 30

No. 100 or No. 140

No. 200

15. The required detection limits for Method 2, Total Metals in Crops; Method 6, DTPA Extractable Metals in Soils; and Method 7, Extractable Arsenic in Soils may conform to the CLP RAS requirements for soils. As relayed by Paula Ausserer / SMO, we understand these limit to be:



SUBJECT _____

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<u>Element</u>	<u>Detection Limit ($\mu\text{g/kg}$)</u>
Cu	50
Fe	50
Zn	10
Mn	15
K	Not spec'd
Pb	5
Cd	1
As	10
Co	50
Cr	10
Ag	10
V	200
Ba	100

I understand these are based on the digestant concentration which is at a standard 50:1 dilution compared to the original soil weight. therefore, standard CLP PAS detection limits are 50x those shown above on a soil weight basis.



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I would like to see lower detection limits, especially for As and Cd but I realize that the laboratories must have an equal basis upon which to bid. The equal bid basis should be the CLP RAS specified detection limits.

Don't worry about the K detection limit as additional dilution may very well be necessary anyway.



SUBJECT _____

BY _____ DATE _____

SHEET NO. _____ OF _____

PROJECT NO. _____

METHOD 11. TOTAL ORGANIC MATTER IN SOILS

1. Performed on soil prepared in accordance with Method 4

2. Method 90-3 attached

Note: This replaces the Method 92-3 previously specified

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METHODS OF SOIL ANALYSIS

Part 2

Chemical and Microbiological Properties

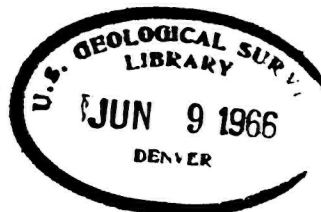
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Number 9 in the series
AGRONOMY

American Society of Agronomy, Inc., *Publisher*
Madison, Wisconsin, USA
1965

90

Organic Carbon¹

L. E. ALLISON

*U. S. Salinity Laboratory, ARS, USDA
Riverside, California*

90-1 GENERAL INTRODUCTION

Carbon is the chief element of soil organic matter that is readily measured quantitatively. Hence, estimates of organic matter frequently are based on organic-C, which is determined mainly by methods of two types: (1) those based on quantitative combustion procedures, wherein C is determined as CO_2 , and (2) those based on the reduction of the $\text{Cr}_2\text{O}_7^{2-}$ ion by organic matter, wherein the unreduced $\text{Cr}_2\text{O}_7^{2-}$ is measured by titration. Organic forms of soil-C plus the carbonate forms of this element, including HCO_3^- and CO_3^{2-} of any soluble salts present, constitute the total-C present in soils. Forms of carbonate and methods of determination are discussed in section 91-1.

Soil organic matter includes: (1) fresh plant and animal residues, capable of rapid decomposition and loss of identity with simultaneous release of nutrient elements; (2) "humus," which represents the vast bulk of resistant organic matter, having high adsorptive capacity for cations and capable of improving soil structure; and (3) inert forms of nearly elemental-C, such as charcoal, coal, or graphite, which are occasionally present in appreciable quantities.

Values for the organic-C content of soils may be expressed as such or may be reported as total organic matter by multiplying the figure for organic-C by the conventional "Van Bemmelen factor" of 1.724. The use of this factor is based on the assumption that soil organic matter contains 58% C. Many studies have been reported on this factor, with highly variable results indicating that it is, at best, only an approximation. Recent studies by Broadbent (1953) indicate that the factor for converting organic-C to organic matter in surface soils is approximately 1.9, and that the factor for subsoils is about 2.5. Since considerable variation exists in the carbon-to-

¹ The assistance of C. D. Moodie and W. B. Bollen in the preparation of this chapter is acknowledged.

organic-matter ratio among different soils, and also among horizons of the same soil, it seems preferable to report organic-C as such.

Two rapid titration methods are described for determining readily oxidizable organic-C, including any other oxidizable substances present in soils. The original method employing external heat was devised by Schollenberger (1927, 1945). Subsequently, Walkley and Black (1934) and Walkley (1946) modified Schollenberger's procedure by the elimination of heating. Both methods involve the digestion of soil in an excess of chromic acid, and the subsequent titration of the excess oxidizing agent. These methods, because of their simplicity and convenience, have been used extensively in lieu of the quantitative wet- and dry-combustion methods, which require more complicated apparatus and a greater time of determination. Since both rapid procedures are subject to incomplete oxidation of C, it is necessary to determine correction factors to bring C data obtained by these methods into agreement with wet- or dry-combustion data for comparative purposes. Rapid titration methods are subject to errors due to the presence in soil of oxidizable substances other than organic-C, such as Cl^- , Fe^{2+} and Mn^{2+} . They have the advantage, however, that the presence of CaCO_3 up to 50% of the sample weight gives no interference.

~~90-2 COMBUSTION METHODS WITH MEASUREMENT OF CARBON DIOXIDE~~

~~90-2.1 Introduction~~

~~Methods for the determination of total-C in soils by wet- or dry-combustion are basic for all quantitative estimates of organic-C. Although the CO_2 evolved may be determined volumetrically, titrimetrically, or gravimetrically, the gravimetric procedure is employed herein. With noncalcareous and unlimed soils, total-C is considered to be organic-C. With calcareous soils, carbonate must be removed before analysis for total-C, or the total-C must be corrected by subtracting carbonate C determined on a separate sample.~~

~~With calcareous soils, the choice between determining organic-C on the sample after removal of carbonate-C, or computing organic-C by subtracting carbonate-C from total-C depends on the need for quantitative data on carbonate-C. If information on carbonate-C is of no interest, then the removal of carbonate from the sample prior to analysis is the more convenient procedure.~~

~~The wet-combustion method for total-C is readily adapted to the removal of carbonate from soils prior to the determination of organic-C. The soil sample can be pretreated in the digestion flask with dilute H_2SO_4 containing FeSO_4 as antioxidant, to remove carbonate and then carried through the determination of total-C without transfer. The FeSO_4 antioxidant prevents~~

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90-2.3.2 PR

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90-2.4.1 SPE

90-2.4.2 PR
Prepare

90-2.7.4 COMMENTS

~~Drying of extracts is best accomplished in 100-ml. flasks of the Kjeldahl type. A 2-liter beaker conveniently holds 4 flasks. Drying in this manner is accomplished more rapidly than the dried samples can be analyzed for organic C.~~

90-3 WALKLEY-BLACK METHOD

90-3.1 Introduction

Oxidizable matter in a soil sample is oxidized by $\text{Cr}_2\text{O}_7^{2-}$, and the reaction is facilitated by the heat generated when 2 volumes of H_2SO_4 are mixed with 1 volume of 1N $\text{K}_2\text{Cr}_2\text{O}_7$ solution. The excess $\text{Cr}_2\text{O}_7^{2-}$ is determined by titration with standard FeSO_4 solution, and the quantity of substances oxidized is calculated from the amount of $\text{Cr}_2\text{O}_7^{2-}$ reduced.

Whereas Schollenberger (1927, 1945) and Allison (1935) used diphenylamine in concentrated H_2SO_4 as indicator, Peech et al. (1947) found that aqueous barium diphenylamine sulfonate is much more stable, equally effective, and has the same blue-to-green color change as diphenylamine. With these indicators, H_3PO_4 is used to sharpen the color change at the endpoint. The o-phenanthroline-ferrous complex indicator (Ferroin) gives a color change from blue to red at a much higher oxidation-reduction potential than either of the diphenylamines and, consequently, it is considered superior to the latter. The use of H_3PO_4 with this indicator appears to be optional; Jackson (1958, p. 211) advises its use, but others (U. S. Salinity Laboratory, 1954) have found it unnecessary. A criticism of o-phenanthroline is that some soils tend to adsorb it, and also that the turbidity caused by some soils tends to obscure the color change at the endpoint. For these reasons, some technicians prefer to filter off the soil, using a small Büchner funnel and a reasonably fast paper, as a means of obtaining a readily observed endpoint.

Smith and Weldon (1941) substituted KMnO_4 in place of indicators by first adding a slight excess of Fe^{2+} titrant to the digestion and then back-titrating the excess Fe^{2+} with standard KMnO_4 to a purple-red endpoint observed over a strong light. In this procedure, only the KMnO_4 needs to be standardized, provided the same volumes of Fe^{2+} and $\text{Cr}_2\text{O}_7^{2-}$ are added to both the blank and the determination.

Potentiometric titrations, using automatic titrators, are entirely suitable for determining the endpoint of the $\text{Cr}_2\text{O}_7^{2-}$ reaction. No H_3PO_4 is required, and the titration proceeds smoothly with a voltage shift at the endpoint of the order of 300 to 400 millivolts for 0.01 to 0.02 ml. of titrant.

Graham (1948) substituted colorimetry for titration in the Walkley-

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90-3 WALKLEY-BLACK METHOD

Black procedure, using the green color of the reduced Cr^{3+} ion as a direct measure of the quantity of C oxidized. The C percentages are read from graphs prepared from C values determined by a quantitative combustion method. Carolan (1948) also used colorimetry but determined the yellow color of the unreduced $\text{Cr}_2\text{O}_7^{2-}$ ion, thereby obtaining an indirect measure of C. Metson (1956) studied both methods extensively and indicated a preference for the Graham modification of the Walkley-Black method.

The highest temperature attained by the heat-of-dilution reaction produced upon addition of the H_2SO_4 is approximately 120°C ., which is sufficient to oxidize the active forms of soil organic-C, but not the more inert forms of C that may be present. This method oxidizes a lower percentage of the total-C present in soils and, moreover, gives a wider range of C recovery than the Schollenberger method (section 90-4). Walkley and Black (1934) obtained 60 to 86% recovery of C, for which a multiplying factor of 1.30 was used. Peech et al. (1947) and Greweling and Peech (1960) reported a similar multiplying factor of 1.33. In a recent study (Allison, 1960) of 16 groups of Walkley-Black C data, which were accompanied by reference C data determined by either wet or dry combustion, the range of C oxidation varied tremendously from one group of soils to another. This oxidation was from a low range of 59 to 74%, averaging 69%, to a high range of 81 to 94% recovery, averaging 86%. The other 14 groups of soils fell between these extremes in range of C recovery. This wide range of C recovery strikingly illustrates the importance, as pointed out by Crowther (1935), of determining a correction factor (f value) for each different group of soils being analyzed by rapid titration methods.

If the Walkley-Black method is modified by applying external heat immediately after adding H_2SO_4 to the sample, the oxidation of organic-C is more nearly complete, and the degree of oxidation is more consistent than in the regular method. By use of the alternative method (section 90-3.2.3) with a group of soils from western USA (U. S. Salinity Laboratory, 1954), a multiplying factor f of $100/89 = 1.12$ was found appropriate.

The Walkley-Black method, and also the Schollenberger method subsequently described in section 90-4, are similarly affected by the presence of readily oxidizable substances other than C. Chlorides, higher oxides of Mn, and reduced Fe may interfere under certain conditions, but their effects can be eliminated or greatly reduced by the exercise of proper precautions (Walkley, 1946). Whereas Fe^{2+} and Cl^- give positive or high values for organic-C, oxides of Mn give negative or low values. The most convenient way to eliminate Cl^- interference is to precipitate the Cl^- as AgCl by adding Ag_2SO_4 to the digestion acid. Other methods consist of washing the soil free of Cl^- prior to analysis, or the application of a correction factor to the apparent C content of the soil. Walkley (1946) found the following relation to be valid up to a ratio of $\text{Cl}/\text{C} = 5$, which is adequate for all but very highly saline soils:

Carbon in soil, % = (Apparent % C in soil) - (% $\text{Cl}^-/12$).

The higher oxides of Mn occur in many forms, but the extent of their occurrence in soils is unknown. The most active type (Walkley, 1946), corresponding to freshly precipitated soil Mn, will take part in oxidation reactions. Active MnO_2 competes with $\text{K}_2\text{Cr}_2\text{O}_7$ when heated in acid media containing oxidizable substances, and thereby induces a negative error of analysis, depending on the quantity present and the extent of its activity. Based on extensive studies of the effect of higher oxides of Mn on the Walkley-Black procedure, Walkley (1946) concluded that in normal soils the quantity of reducible oxides of Mn is invariably small, and that in highly manganiferous soils only a small fraction of all oxides present is in the active state capable of competing with $\text{Cr}_2\text{O}_7^{2-}$ oxidation. Moreover, all errors observed in this study from the effect of soil Mn on the C determination were <6%. Walkley (1946) devised a procedure for determining the quantity of reactive oxygen in soils if large quantities of reactive Mn are encountered.

Ferrous iron, if present in the soil sample, would be oxidized by $\text{Cr}_2\text{O}_7^{2-}$ and thereby would give a positive error in the analysis, i.e., high values of organic-C. Traces of Fe^{2+} are known to exist in well-aerated soil, and appreciable amounts of this constituent may be found in soils rich in organic matter or in paddy soils. Lee (1939) obtained highly erroneous C values on gleied subsoils from paddy land by the rapid titration method. However, Walkley (1946) obtained normal C recovery from gleied soils that were thoroughly air dried for 1 or 2 days before analysis, in which case the amount of soluble Fe^{2+} compounds is trifling compared to the quantity of organic-C present. It is advisable to avoid grinding soil samples, particularly coarse-textured soils, in iron or steel equipment to avoid the positive errors of analysis that will result from contaminating the samples with metallic (reduced) iron.

90-3.2 Method ²

90-3.2.1 REAGENTS

1. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), 1N: Dissolve 49.04 g. of reagent-grade $\text{K}_2\text{Cr}_2\text{O}_7$ (dried at 105°C.) in water, and dilute the solution to a volume of 1,000 ml.
2. Sulfuric acid (H_2SO_4), concentrated (not less than 96%). If Cl^- is present in the soil, add Ag_2SO_4 to the acid at the rate of 15 g. per liter.
3. Orthophosphoric acid (H_3PO_4), concentrated.
4. *o*-phenanthroline-ferrous complex, 0.025M: Dissolve 14.85 g. of *o*-phenanthroline monohydrate and 6.95 g. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water, and dilute the solution to a volume of 1,000 ml. *o*-phenanthroline-

² Walkley, 1946; Peech, et al., 1947; Greweling and Peech, 1960.

Cl⁻ will be present so add this reagent

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90-3 WALKLEY-BLACK METHOD

ferrous complex is available under the name of "Ferrouin" from the G. Frederick Smith Chemical Co., Station D, Box 5906, 867 McKinley Ave., Columbus 22, Ohio.

5. Barium diphenylamine sulfonate: Prepare a 0.16% aqueous solution. This reagent is an optional substitute for No. 4.
6. Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) solution, 0.5N: Dissolve 140 g. of reagent-grade $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water, add 15 ml. of concentrated H_2SO_4 , cool the solution, and dilute it to a volume of 1,000 ml. Standardize this reagent daily by titrating it against 10 ml. of 1N $\text{K}_2\text{Cr}_2\text{O}_7$, as directed below. (For routine use, this reagent in larger quantities may be stored under hydrogen from a Kipp generator with negligible change in titer from day to day.)

90-3.2.2 PROCEDURE

Grind the soil to pass a 0.5-mm. sieve, avoiding iron or steel mortars. Transfer a weighed sample, containing 10 to 25 mg. of organic-C, but not in excess of 10 g. of soil, into a 500-ml. wide-mouth Erlenmeyer flask. Add 10 ml. of 1N $\text{K}_2\text{Cr}_2\text{O}_7$, and swirl the flask gently to disperse the soil in the solution. Then rapidly add 20 ml. of concentrated H_2SO_4 , directing the stream into the suspension. Immediately swirl the flask gently until soil and reagents are mixed, then more vigorously for a total of 1 minute. Allow the flask to stand on a sheet of asbestos for about 30 minutes. Then add 200 ml. of water to the flask, and filter the suspension if experience shows that the endpoint of the titration cannot otherwise be clearly discerned. Add 3 to 4 drops of *o*-phenanthroline indicator, and titrate the solution with 0.5N FeSO_4 . As the endpoint is approached, the solution takes on a greenish cast and then changes to dark green. At this point, add the ferrous sulfate drop by drop until the color changes sharply from blue to red (maroon color in reflected light against a white background). Make a blank determination in the same manner, but without soil, to standardize the $\text{Cr}_2\text{O}_7^{2-}$. Repeat the determination with less soil if more than 75% of the dichromate is reduced.

Calculate the results according to the following formula, using a correction factor $f = 1.33$ or a more suitable value found experimentally:

Organic-C, % =

$$\frac{(\text{Milliequivalents } \text{K}_2\text{Cr}_2\text{O}_7 - \text{milliequivalents } \text{FeSO}_4) \times 0.003 \times 100}{\text{Grams water-free soil}} \times (f).$$

~~90-3.2.3 ALTERNATIVE PROCEDURE USING EXTERNAL HEAT~~

~~Proceed in the manner described in section 90-3.2.2 through the operation of adding 20 ml. of concentrated H_2SO_4 . Insert a 200°C. thermometer into the reaction mixture, and gently heat the flask over a low flame to attain a temperature of 150°C. in a heating period of approximately 1~~

90-5 LITERATURE CITED

- Allison, L. E. 1935. Organic soil carbon by reduction of chromic acid. *Soil Sci.* 40:311-320.
- Allison, L. E. 1960. Wet combustion apparatus and procedure for organic and inorganic carbon in soil. *Soil Sci. Soc. Am. Proc.* 24:36-40.
- Bremner, J. M. 1949. Use of the Van Slyke-Neil manometric apparatus for the determination of organic and inorganic carbon in soil and of organic carbon in soil extracts. *Analyst* 74:492-498.
- Broadbent, F. E. 1953. The soil organic fraction. *Advan. Agron.* 5:153-183.
- Carolan, R. 1948. Modification of Graham's method for determining soil organic matter by colorimetric analysis. *Soil Sci.* 66:241-247.
- Crowther, E. M. 1935. First report of the organic carbon committee. *Trans. Intern. Congr. Soil Sci.* 3rd Oxford, 1935. 1:114-126.
- Graham, E. R. 1948. Determination of soil organic matter by means of a photoelectric colorimeter. *Soil Sci.* 65:181-183.
- Greweling, T., and Peech, M. 1960. Chemical soil tests. *Cornell Univ. Agr. Exp. Sta. Bull.* 960.
- Jackson, M. L. 1958. *Soil Chemical Analysis*. Prentice-Hall, Inc., Englewood Cliffs, N. J.
- Lee, C. K. 1939. The determination of organic matter in paddy soils. The reliability of rapid titration methods. *Ind. Eng. Chem. Anal. Ed.* 11:428.
- Metson, A. J. 1956. Methods of chemical analysis for soil survey samples. *New Zealand Dept. Sci. & Ind. Res., Soil Bur. Bull.* 12.
- Peech, M., Dean, L. A., and Reed, J. 1947. Methods of soil analysis for soil fertility investigation. *U. S. Dept. Agr. Circ.* 757.
- Piper, C. S. 1942. *Soil and Plant Analysis*, pp. 221-222. Interscience Publishers Inc., New York.
- Schollenberger, C. J. 1927. A rapid approximate method for determining soil organic matter. *Soil Sci.* 24:65-68.
- Schollenberger, C. J. 1945. Determination of soil organic matter. *Soil Sci.* 59:53-56.
- Smith, H. W., and Weldon, M. D. 1941. A comparison of some methods for the determination of soil organic matter (1940). *Soil Sci. Soc. Am. Proc.* 5:177-182.
- United States Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. *U. S. Dept. Agr. Handbook* 60.
- Walkley, A., and Black, I. A. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Sci.* 37:29-38.
- Walkley, A. 1946. A critical examination of a rapid method for determining organic carbon in soils—effect of variations in digestion conditions and of inorganic soil constituents. *Soil Sci.* 63:251-263.

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